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(54) **Galvanic-cell gas sensor**

Galvanische Zelle als Gassensor

Capteur de gaz à cellule galvanique

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Description

[0001] This invention relates to a galvanic-cell gas sensor comprising a cathode and an anode adapted to come into contact with a gas to be detected and sealed in an electrolyte.

[0002] A conventional galvanic-cell gas sensor comprises a holder serving as a container to hold an acid electrolyte and having a window and a diaphragm of a water-repellent film of a macromolecular fluorochemical sealed therein, with a cathode of gold (Au) disposed in a segment holding the electrolyte and an anode of lead (Pb) disposed apart from the cathode.

[0003] This type of sensor holding an electrolyte has been required to have a liquid-tightness that in turn calls for a complex sealing structure. The use of lead as the unnecessarily large anode has made it extremely difficult to reduce the size of the container.

[0004] The anode A has a rod portion B at one end thereof formed by casting or other method or a rod B' of a metal having a high corrosion resistance to the electrolyte and planted on the anode, as shown in Fig. 5. Therefore, the anode has been disproportionately considering the service life of the sensor and hampered the size reduction of the sensor.

[0005] WO-A-9922229 discloses a volume efficient acid-based galvanic oxygen sensor.

[0006] According to the invention there is provided a galvanic-cell gas sensor comprising a casing containing a diaphragm permitting the permeation of gas to be detected but having a water-repelling property, and a cathode provided on the back side of the diaphragm, an anode, and a sheet impregnated with an electrolyte and disposed between said cathode and anode, with said diaphragm positioned so as to be exposed to the atmosphere, characterized by said anode being formed a electrolytic coating of a layer of lead on a conductive material having a corrosion resistance to electrolyte, the coating formed so as to leave a portion thereof uncoated to serve as a lead.

[0007] This galvanic-cell gas sensor eliminates the need to form the lead segment on the anode from lead sheet while permitting to reduce the sensor size by coating an appropriate amount of lead proportional to the sensor life on the anode through accurate control of coating time.

[0008] Thus, the object of this invention is to provide a galvanic-cell gas sensor of smaller size by making the anode size proportional to the sensor life.

[0009] In the Drawings:

Fig. 1 is a cross-sectional view of an embodiment of a galvanic-cell gas sensor according to this invention. Fig. 2 is a perspective view of component elements, notably an electrode-holding frame, of the same gas sensor. Figs. 3(a) and 3(b) show the top and bottom conducting patterns of a circuit board mounted in the same gas sensor. Figs. 4(a) and 4

(b) are cross-sectional views of a substrate making up the anode and an embodiment of the anode. Fig. 5 is a perspective view showing an example of the conventional anode.

[0010] Fig. 1 shows a galvanic-cell gas sensor according to this invention. An electrode-holding frame 1 consisting of a closed-end cylinder has a through hole 3 at the center of the top thereof. The through hole 3 having a diameter substantially equal to the outside diameter of a cathode 2 is adapted to hold the cathode 2 therein with the top of the cathode 2 protruding somewhat above the top edge thereof, as shown in Fig. 2. A cathode 2 whose top surface 2a is convexly shaped is put in the upper part of the through hole 3 in the electrode-holding frame 1. A lead 4 is run from the cathode 2 to the bottom of the electrode-holding frame 1 over the top and peripheral surfaces thereof. The lead 4 is pulled out to run in the nonradial direction over the top surface 1a of the electrode-holding frame 1 and held in contact therewith over a relatively long distance.

[0011] A sheet 5 to hold an electrolyte and an anode 6 described later are laminated on the rear side of the electrode-holding frame 1. A lead 7 is pulled from the anode 7 through a through hole 1b in the electrode-holding frame 1 so as to run somewhat off the radial direction as shown in Fig. 2.

[0012] To the top surface of the electrode-holding frame 1 is fastened a gas-permeable water-repellent film 8, such as a film of propylene fluoride copolymer, whose diameter is somewhat smaller than the diameter of the electrode-holding frame 1 and larger than that of the through hole 3 with an adhesive bond applied to the outer edge thereof. An annular groove 1c provided outside the through hole 3 takes in any excess adhesive bond so as to prevent the adhesive bond from flowing into the cathode 2.

[0013] A closed-end cap 10 having a center through hole 9 of electrically insulating material, such as rubber, is placed over the water-repellent film 8. The rear surface of the cap 10 is concaved with respect to the top surface of the electrode-holding frame 1, while the cathode 2 having a substantially convex surface is placed so as to lie substantially flush with the top surface 1a. As such, the water-repellent film 8 becomes spherically curved when pressed under the cap 10.

[0014] In this state, the lead 7 of the anode 6 pulled out through the through hole 1b in the top surface 1a of the electrode-holding frame 1 and a through hole 10a in the top corner of the cap 10 is run over the top surface of the cap 10 to a point opposite the lead 4 of the cathode 2 (as designated by reference numeral 7' with a dot-dash line in Fig. 2). Then, the lead 7 is bent so as to run along the peripheral surface of the cap 10 and taken in through a notch 10b. The lead 7 thus detoured establishes a definite conductive relationship with the metal cap proper 13 by increasing the area of contact therewith to a maximum.

[0015] A sealing film 12 of macromolecular substance, such as a film of tetrafluoroethylene copolymer, fit against a stepped part 1d formed in the opening of the electrode-holding frame and held by the metal cap proper 13 having a window 13a facing the cathode 2 defines a space to hold the electrolyte outside of which a circuit board 14 is provided.

[0016] The circuit board 14 has conducting patterns 15 and 16 on the surface thereof facing the anode 6 that are adapted to be connected to the leads 4 and 7 of the cathode 2 and anode 6 as shown in Fig. 3(a). The reverse side of the circuit board 14 has an annular conductive pattern 16' to connect to the anode 6 along the periphery thereof and a terminal conductive pattern 15' to connect to the cathode 2 in the center thereof. A relay terminal 17, to which a temperature-compensating thermal sensing resistor R1 and an output standardizing relay R2 are connected, is provided between the conductive patterns 15' and 16'.

[0017] A metal bottom cap 18 is fit in the cap 10 whose inside diameter is substantially equal to the outer periphery of the metal bottom cap 18. An annular electrically insulating plate 19 is provided around the metal bottom cap 18 to caulk the opening in the metal cap 13.

[0018] Thus, the anode 6 establishes a conductive relationship with the metal cap proper 13 by means of the lead 7 that comes into contact with the bottom and inner wall and the bottom of the top surface of the metal cap proper 13, while the cathode 2 establishes a conductive relationship by means of the metal bottom cap 18 that resiliently comes into contact with the annular conductive pattern 16' on the circuit board 14. Therefore, the sensor output can be taken out from the side and bottom of the cap, as with a button cell.

[0019] Fig. 4 shows an embodiment of the anode 6 described earlier. A sheet of material having a corrosion resistance to the electrolyte, good workability and electrical conductivity, and having no electrochemical action on the anode, such as nickel, is formed, by stamping or etching, into a piece comprising an annular electrode segment 20 and the lead 7, as shown in Fig. 4(a). Then, a layer of lead 21 of amount appropriate for the sensor life is coated on the electrode segment as shown in Fig. 4(b).

[0020] This layer of lead 21 is formed by using a plating bath comprising, for example, 200 parts PbCO_3 , 100 parts HBF_4 , 15 parts H_3BO_3 , and 0.2-0.5 part gelatin, with the portion to be used as the lead 7 not immersed in the bath or kept out of contact therewith by using a resist medium. The anode 6 having the lead 7 not coated with lead is formed by controlling the amount of lead coated on the electrode segment 20 by passing an electric current for a time corresponding to the amount of electric charge appropriate for the sensor life.

[0021] The electrolyte is either preliminarily impregnated into the sheet 5 or poured into a hollow space 11 through an opening in the electrode-holding frame 1 before the circuit board 1 is placed in position.

Claims

1. A galvanic-cell gas sensor comprising a casing containing a diaphragm (8) permitting the permeation of gas to be detected but having a water-repelling property, a cathode (2) provided on the back side of the diaphragm, an anode (6), and a sheet (5) impregnated with an electrolyte and disposed between said cathode and anode, with said diaphragm positioned so as to be exposed to the atmosphere, **characterized by** said anode being formed from an electrolytic coating of a layer of lead on a conductive material having a corrosion resistance to electrolyte, the coating formed so as to leave a portion thereof uncoated to serve as a lead (7).
2. A galvanic-cell gas sensor according to claim 1, in which said cathode (2) has a convexly shaped top surface and is fitted in the upper part of a through-hole (3) at the center of a closed-end cylindrical electrode-holding frame (1), and said diaphragm (8) is mounted on top of said electrode-holding frame and curved along said convexly shaped top surface of the cathode under the pressure of a cap (10) of elastic material having a center through-hole (9).
3. A galvanic-cell gas sensor according to claim 2, in which an annular groove is provided outside the through hole (3) in the electrode-holding frame (1) and said diaphragm (8) is fastened to said electrode-holding frame with an adhesive outside said groove.
4. A galvanic-cell gas sensor according to claim 2, in which said anode (6) is contained in the closed-end cylindrical portion of said electrode-holding frame (1), said lead (7) extends from said electrode-holding frame, is resiliently held between the top surface of said electrode-holding frame and said cap (10), and passes outside through a hole in said cap, and a lead connected to said anode is held between said electrode-holding frame and said cap and leads outward.
5. A galvanic-cell gas sensor according to claim 4, in which the lead (7) of said anode (6) is held in contact with a conductive casing (13), the other end of the lead of said cathode (2) is connected to a circuit board (14) and in contact with a conductive bottom cap (18) constituting part of said casing through a conductive pattern on said circuit board, and said conductive case (13) and cap (18) are insulated from each other and fastened by caulking (19).
6. A galvanic-cell gas sensor according to claim 5, in which said circuit board (14) has a conductive pattern to be connected to said cathode (2) provided along the periphery of the surface thereof facing said bottom cap (18) and a resistance connected to said anode (6) and cathode.

Patentansprüche

1. Galvanikzellen-Gassensor, umfassend,
ein Gehäuse, das eine Membrane (8) enthält, die die
Permeation des zu erfassenden Gases erlaubt, aber
eine Wasser abweisende Eigenschaft aufweist,
eine Kathode (2), die auf der Rückseite der Mem-
brane vorgesehen ist,
eine Anode (6) und ein Lagenelement (5), das mit
einem Elektrolyt imprägniert ist und zwischen der
Kathode und der Anode angeordnet ist, wobei die
Membrane so angeordnet ist, dass sie der Atmo-
sphäre ausgesetzt ist,
dadurch gekennzeichnet, dass die Anode aus ei-
ner elektrolytischen Beschichtung einer Schicht von
Blei auf einem leitfähigen Material mit einer Korrosi-
onsbeständigkeit gegenüber dem Elektrolyt gebildet
ist, wobei die Beschichtung so gebildet ist, dass sie
einen Bereich davon unbeschichtet lässt, um als An-
schlussleitung (7) zu dienen. 5
2. Galvanikzellen-Gassensor gemäß Anspruch 1, wo-
bei die Kathode (2) eine konvexe obere Fläche auf-
weist und in den oberen Teil einer Durchgangsöff-
nung (3) in der Mitte eines abgeschlossenen Endes
eines zylindrischen Elektrode-Halterahmens (1) ein-
gepasst ist, und wobei die Membrane (8) oben auf
dem Elektrode-Halterahmen angebracht ist und ent-
lang der konvex geformten oberen Fläche der Ka-
thode unter dem Druck einer Abdeckung (10) aus
elastischem Material, die eine zentrale Durchgangs-
öffnung (9) aufweist, gekrümmt ist. 10
3. Galvanikzellen-Gassensor gemäß Anspruch 2, wo-
bei eine ringförmige Nute außerhalb der Durch-
gangsöffnung (3) in dem Elektrode-Halterahmen (1)
vorgesehen ist, und wobei die Membrane (8) an dem
Elektrode-Halterahmen mit einem Klebemittel au-
ßerhalb der Nute befestigt ist. 15
4. Galvanikzellen-Gassensor gemäß Anspruch 2, wo-
bei die Anode (6) in dem abgeschlossenen Ende des
zylindrischen Bereichs des Elektrode-Halterahmens
(1) enthalten ist, wobei die Anschlussleitung (7) sich
von dem Elektrode-Halterahmen weg erstreckt, zw-
ischen der oberen Fläche des Elektrode-Halterah-
mens und der Abdeckung (10) elastisch gehalten ist,
und durch eine Öffnung in der Abdeckung nach drau-
ßen führt, und eine Anschlussleitung, die mit der An-
ode verbunden ist, zwischen dem Elektroden-Halte-
rahmen und der Abdeckung gehalten wird und nach
draußen führt. 20
5. Galvanikzellen-Gassensor gemäß Anspruch 4, wo-
bei die Anschlussleitung (7) der Anode (6) mit einem
leitfähigen Gehäuse (13) in Kontakt gehalten wird,
das andere Ende der Anschlussleitung der Kathode
(2) mit einer Leiterplatte (14) verbunden ist und mit
einer leitfähigen Bodenabdeckung (18), die einen
Teil des Gehäuses bildet, über ein leitfähiges Muster
auf der Leiterplatte in Kontakt ist, und das leitfähige
Gehäuse (13) und die Abdeckung (18) gegeneinan-
der isoliert sind und durch Verstemmen (19) befestigt
sind. 25
6. Galvanikzellen-Gassensor gemäß Anspruch 5, wo-
bei die Leiterplatte (14) ein mit der Kathode (2) zur
verbindendes leitfähiges Muster, das entlang der
Peripherie der Oberfläche davon, die der Bodenab-
deckung (18) gegenüberliegt, vorgesehen ist, und
einen Widerstand, der mit der Anode (6) und Katho-
de verbunden ist, aufweist. 30

Revendications

1. Capteur de gaz à cellule galvanique comprenant un
boîtier contenant un diaphragme (8) permettant la
perméation de gaz à détecter mais ayant une pro-
priété hydrophobe, une cathode (2) prévue sur le
côté arrière du diaphragme, une anode (6) et une
feuille (5) imprégnée d'un électrolyte et placée entre
ladite cathode et ladite anode, avec ledit diaphragme
positionné de manière à être exposé à l'atmosphère,
caractérisé en ce que ladite anode est formée d'un
revêtement électrolytique d'une couche de plomb
sur un matériau conducteur ayant une résistance à
la corrosion à l'électrolyte, le revêtement étant formé
pour laisser une partie de ce dernier non recouverte
pour servir de conducteur (7). 35
2. Capteur de gaz à cellule galvanique selon la reven-
dication 1, dans lequel ladite cathode (2) possède
une surface supérieure de forme convexe et est pla-
cée dans la partie supérieure d'un orifice de passage
(3) au centre d'un cadre de maintien d'électrode cy-
lindrique à extrémité fermée (1), et ledit diaphragme
(8) est monté au-dessus dudit cadre de maintien
d'électrode et incurvé le long de ladite surface su-
périeure de forme convexe de la cathode sous la
pression d'un capuchon (10) de matériau élastique
possédant un orifice de passage central (9). 40
3. Capteur de gaz à cellule galvanique selon la reven-
dication 2, dans lequel une rainure annulaire est four-
nie à l'extérieur de l'orifice de passage (3) dans le
cadre de maintien d'électrode (1) et ledit diaphragme
(8) est fixé audit cadre de maintien d'électrode avec
un adhésif à l'extérieur de ladite rainure. 45
4. Capteur de gaz à cellule galvanique selon la reven-
dication 2, dans lequel ladite anode (6) est contenue
dans une partie cylindrique à extrémité fermée dudit
cadre de maintien d'électrode (1), ledit conducteur
(7) s'étend depuis ledit cadre de maintien d'électro-
de, est maintenu de manière élastique entre la sur-
face supérieure de ladite cathode et la surface infé-
rieure de ladite anode, et ladite anode est maintenue
de manière élastique entre la surface supérieure de
ladite cathode et la surface inférieure de ladite anode.
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face supérieure dudit cadre de maintien d'électrode et ledit capuchon (10), et passe à l'extérieur à travers un orifice dans ledit capuchon, et un conducteur connecté à ladite anode est maintenu entre ledit cadre de maintien d'électrode et ledit capuchon et se dirige vers l'extérieur. 5

5. Capteur de gaz à cellule galvanique selon la revendication 4, dans lequel le conducteur (7) de ladite anode (6) est maintenu en contact avec un boîtier conducteur (13), l'autre extrémité du conducteur de ladite cathode (2) est connecté à une carte de circuit imprimé (14) et en contact avec un capuchon inférieur conducteur (18) faisant partie dudit boîtier par un motif conducteur sur ladite carte de circuit imprimé, et ledit boîtier conducteur (13) et le capuchon (18) sont isolés l'un de l'autre et fixés par matage (19). 10 15

6. Capteur de gaz à cellule galvanique selon la revendication 5, dans lequel ladite carte de circuit imprimé (14) possède un motif conducteur destiné à être connecté à ladite cathode (2), prévu le long de la périphérie de la surface de celle-ci en face dudit capuchon inférieur (18) et une résistance connectée à ladite anode (6) et à la cathode. 20 25

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FIG. 1

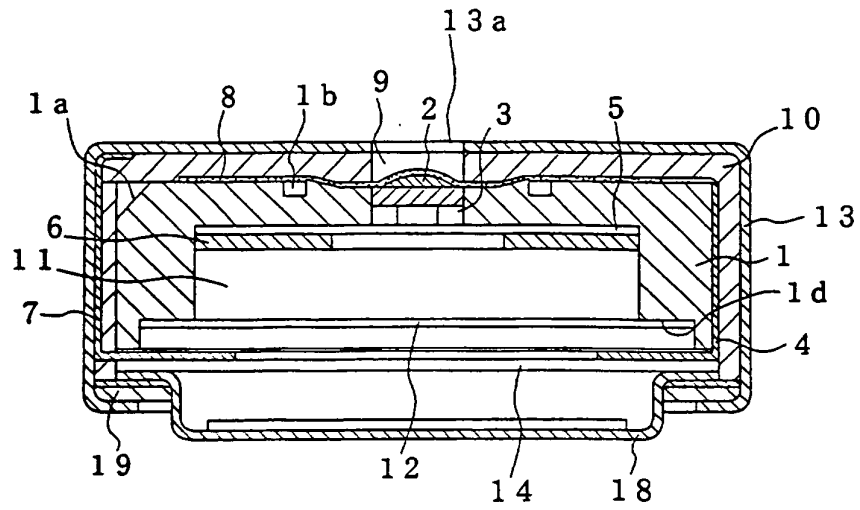


FIG. 2

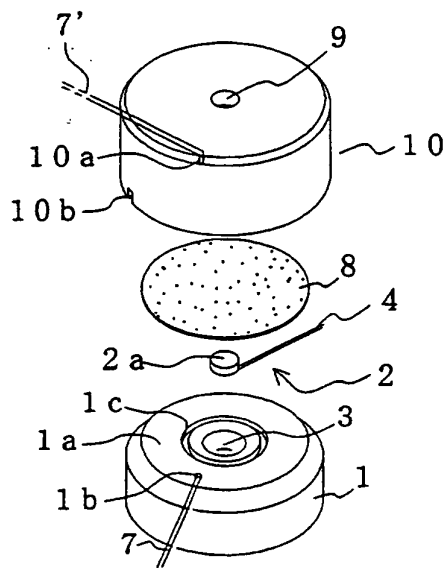


FIG. 3 (a)

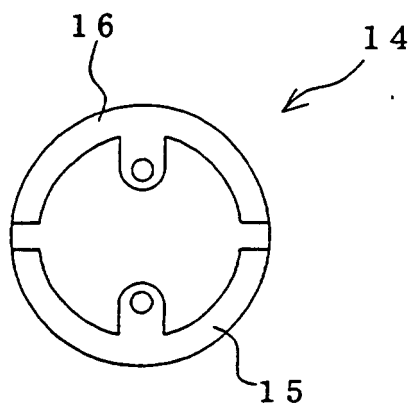


FIG. 3 (b)

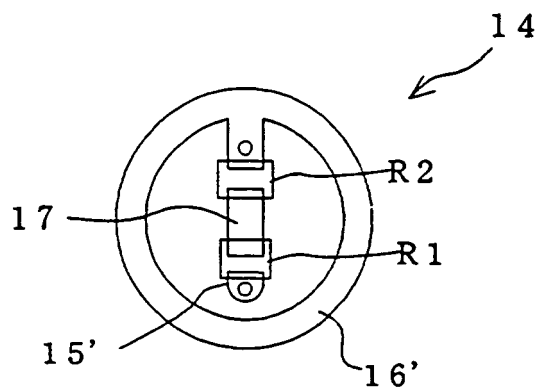


FIG. 4 (a)

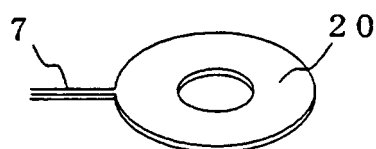


FIG. 4 (b)

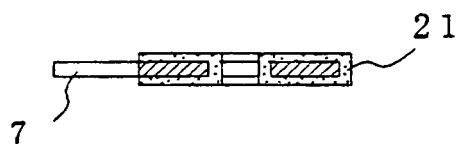


FIG. 5

PRIOR ART

